



Short communication

A direct methanol fuel cell without the use of a polymer electrolyte membrane or precious metal cathode catalyst

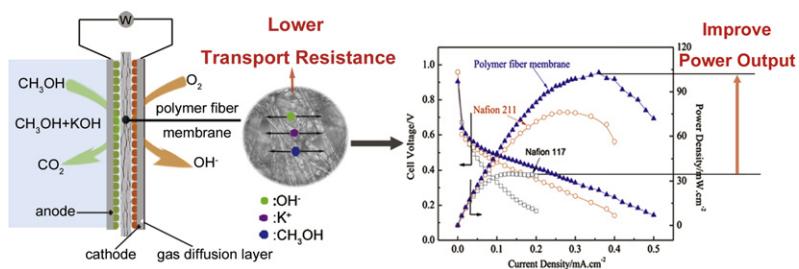
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HIGHLIGHTS

- Polymer fiber membranes (PFMs) are electrolyte-permeable.
- A novel DMFC structure is fabricated using PFM as separator.
- The LaNiO_3 cathode demonstrates excellent tolerance to methanol-poisoning.
- The LaNiO_3 cathode demonstrates excellent stability throughout a 110-h test.
- The peak power density of DMFC with PFM can reach 103 mW cm^{-2} at 65°C .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 October 2012

Received in revised form

21 January 2013

Accepted 22 January 2013

Available online 9 February 2013

Keywords:

Direct methanol fuel cells

Polymers

Membranes

Perovskite phases

ABSTRACT

Direct methanol fuel cells (DMFCs) are a promising power source for mobile devices. However, DMFCs currently experience the technical shortcomings of high cost due to the use of noble metal catalysts and polymer electrolyte membranes (PEMs), low power density because of their low catalytic efficiency and cathode catalyst poisoning by methanol, which crosses through the PEM from anode to cathode. Here, we report a new DMFC structure utilizing a polymer fiber membrane (PFM), which is electrolyte-permeable, instead of a PEM. An inexpensive perovskite-type oxide, LaNiO_3 , is used as the cathode catalyst, which has shown excellent tolerance to methanol-poisoning and good catalytic activity for oxygen reduction reaction (ORR). The peak power density can reach 103 mW cm^{-2} at 65°C . This improvement in performance is due to the lower electrical resistance of the PFM.

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1. Introduction

Fuel cells have been the subject of many studies due to growing concerns about global warming, the exhaustion of fossil fuels and increasing energy demands. As a promising alternative to hydrogen fuel cells, direct methanol fuel cells (DMFCs) are a type of fuel cells that use liquid methanol as fuel, which converts chemical energy directly into electricity while causing little pollution. Their possible

application in mobile devices is attractive because of the high energy density of liquid methanol and its ease of transportation. Moreover, compared with hydrogen fuel, methanol has the advantage of circumventing the hydrogen storage problem [1,2] and avoiding the construction of infrastructures for dispensing liquid fuel because they are already in place [3].

However, DMFCs are not yet commercially viable, largely because polymer electrolyte membranes (PEMs) allow methanol crossover from the anode to the cathode. The methanol is catalyzed into carbon dioxide by the cathode catalysts, such as Pt or Pt-alloy. Because of this crossover, the reaction electrons do not pass into the circuit and are instead consumed by the oxygen reduction reaction

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(ORR) producing OH^- at the cathode. This process not only wastes fuel but also creates a “mixed potential” at the cathode. Moreover, the cathode catalysts, especially noble metal catalysts, will be poisoned by the methanol.

To overcome this issue and achieve acceptable power output, various methods have been studied, such as the use of selective cathode catalysts for ORR that have limited methanol oxidation activity. Catalysts such as $\text{Ru}_3\text{Se}_2\text{Mo}_{0.08}$ [3], $\text{Pt-TiO}_2/\text{C}$ [4], Pt-Au/C [4], Ir-Se chalcogenide [5], $\text{Ir}_x\text{Co}_{1-x}/\text{C}$ [6], ordered mesoporous platinum graphitic carbon [7] and ordered mesoporous carbon nitride [8] have ORR catalytic activity as well as methanol tolerance.

Another approach to this problem is to improve of the Nafion membrane by adding inorganic compounds to limit methanol crossover; however, the price of the PEM remains high [9]. Other types of membranes, such as hydrocarbon membranes, were also studied to for use in DMFCs, showing lower methanol crossover and higher conductivity and stability than Nafion [9–11]. However, few of these membranes can satisfy the technical targets of the Department of Energy (DOE): a cost of $<20 \text{ } \text{S m}^{-2}$, membrane conductivity of $>0.07 \text{ S cm}^{-1}$ at $20 \text{ }^\circ\text{C}$ and durability for >2000 cycles [12].

Recently, a polymer fiber membrane (PFM) was used to replace PEM in direct borohydride fuel cells [13]. PFM is electrolyte-permeable and offers electrical isolation between the cathode and anode. The application of PFM in direct borohydride fuel cells not only lowers the cost but also improves the power output. For these reasons, PFM were used in the DMFCs in this work. A promising performance was achieved using the new DMFCs structure.

2. Experimental

2.1. Catalysts

The LaNiO_3 perovskite catalyst was prepared by citrate-based sol–gel method as described in Ref. [14]. PtRu/C (HiSpec 10000) was purchased from Johnson Matthey. PFM was purchased from Nippon Kodoshi Corporation and its physical properties are presented in our previous work [13].

2.2. Electrochemical catalyst measurements

The electrochemical characterization of the catalysts was performed using a rotating disk electrode (RDE, Pine Research Instrumentation) connected to an electrochemical workstation (CHI750D, CH Instruments) with an AFMSRCE rotator (Pine Research Instrumentation). A Hg/HgO (1 M KOH) electrode and Pt net ($1 \times 1 \text{ cm}^2$) were used as the reference and counter electrodes, respectively. The working electrode, RDE, was modified by the catalysts as follows. First, a catalyst ink was prepared by ultrasonically mixing 3 mg of the catalyst, 2 ml of deionized water, 0.5 ml of isopropanol and 50 μl of Nafion (5 wt.%) into a slurry and then spreading 5 μl of the slurry onto the surface of a glassy carbon electrode, which was allowed to dry overnight. The electrolyte solution (1 M KOH) was either saturated or purged of oxygen by bubbling oxygen or nitrogen gas, respectively, for 30 min before the tests. The capacitive current was measured in the oxygen-removed solution.

The working electrode was scanned cathodically at a rate of 5 mV s^{-1} in an RDE experiment with rotating speeds from 400 rpm to 2500 rpm. The apparent number of electrons transferred (n) during the ORR was calculated by the slopes of Koutecky–Levich (K–L) plots [15]. The K–L equation is

$$\frac{1}{J} = \frac{1}{J_l} + \frac{1}{J_k}$$

$$J_k = FAkC^0$$

$$J_l = 0.62nFAD_{\text{O}_2}^{2/3}\nu^{-1/6}C^0\omega^{1/2}$$

where J_k is the kinetic current, J_l is the diffusion-limiting current, n is the overall number of transferred electrons during O_2 reduction, F is the Faraday constant (96,500 C mol $^{-1}$), A is the geometric area of the electrode (cm^2), k is the rate constant for oxygen reduction, C^0 is the saturated O_2 concentration in the electrolyte, D_{O_2} is the diffusion coefficient of O_2 in the electrolyte, ν is the kinetic viscosity of the solution, and ω is the angular frequency of the rotation in terms of rad s^{-1} .

J_k can then be calculated based on the following equation:

$$J_k = \frac{J \times J_l}{J_l - J}$$

The kinetic current was normalized to the catalyst loadings to obtain the mass activities.

2.3. Preparation of cathodes and anodes

The cathode for the DMFCs with PFM consisted of a gas diffusion layer, a current collector and an active layer. To prepare the gas diffusion layer, 60 wt.% acetylene black and 40 wt.% polytetrafluoroethylene (PTFE) (60 wt.% PTFE solution) were mixed into a slurry. The slurry was then pressed into a 0.3 mm membrane and heated at $340 \text{ }^\circ\text{C}$ for 1 h. A non-noble metal catalyst ink was prepared by mixing 30 wt.% catalyst, 45 wt.% carbon nanotubes and 25 wt.% PTFE (60 wt.% PTFE solution). Next, the ink was smeared onto a current collector (nickel foam) and dried at $80 \text{ }^\circ\text{C}$ for 2 h under vacuum. The cathode was finished by pressing the gas diffusion layer and the prepared current collector under 2 MPa of pressure.

The cathode for the DMFCs with Nafion membranes was prepared by smearing the catalyst ink onto a hydrophobic-treated carbon cloth, which was dried at $80 \text{ }^\circ\text{C}$ for 2 h under vacuum. Finally, the cathode was pressed under 2 MPa of pressure. The loading of non-noble metal cathode catalyst was ca. 7.5 mg cm^{-2} .

The DMFC anodes were prepared in the same way regardless of whether PFM or Nafion membranes were used. First, 10 mg cm^{-2} PtRu/C and 3 wt.% PTFE were mixed together. Next, the mixture was pasted onto the nickel foam and dried at $80 \text{ }^\circ\text{C}$ for 2 h under vacuum. Finally, the anode electrode was pressed under 3 MPa of pressure. The PtRu loading in anode was 6 mg cm^{-2} .

2.4. DMFC structure

An electrolyte-permeable membrane was used between the cathode and anode in DMFC. As shown in Fig. 1, PFM was used as the permeable membrane instead of PEM. The fiber materials in the PFM can be polypropylene or polyamide or polyvinyl alcohol and its function is to electrically insulate the cathode and anode. PFM has good wettability and is easily saturated by aqueous solution. Therefore, the PFM in DMFCs acts as a very thin liquid electrolyte layer and allows the ions and methanol molecules to cross freely. In this arrangement, the cathode catalysts can contact methanol freely and it requires that the cathode catalysts decompose oxygen in methanol solution while being inert to the methanol oxidation.

In addition to this DMFC structure, a special design was employed in the cathode: a gas diffusion layer was built on the side

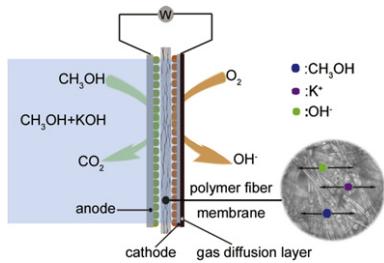


Fig. 1. Schematic diagrams of the DMFC with a polymer fiber membrane (PFM). LaNiO₃/CNT and PtRu/C acted as the cathode and anode catalysts, respectively.

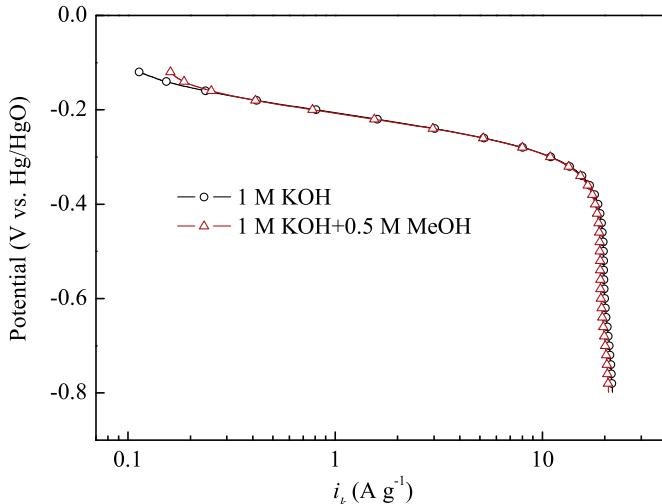


Fig. 2. Tafel plot of the ORR activity of the LaNiO₃ modified RDE, measured with or without methanol in KOH solution. All of the activities are transport-compensated, capacitive-corrected and normalized to the catalyst loading.

of the cathode opposite the catalyst, which allows the transportation of oxygen gas to the catalyst while hindering the permeation of the liquid fuel into the oxygen flow field. The main function of the gas diffusion layer is providing a sufficient three phase area for ORR.

LaNiO₃ was chosen as cathode catalyst due to its excellent ORR activity in alkaline solution [16]. However, to ensure that LaNiO₃ can be used in this DMFC structure, its methanol tolerance was measured. As shown in Fig. 2, although the activity of LaNiO₃ is slightly lower in methanol alkaline solution than in pure alkaline

solution in the high-overpotential region, the Tafel plots measured with or without methanol in KOH solution show very similar polarization tendencies, which indicate that LaNiO₃ has good methanol tolerance. Therefore, we tentatively employed LaNiO₃/CNT as the cathode catalyst in this DMFC.

2.5. Fuel cell testing

In this fuel cell structure, the cathode was in contact with the oxygen parallel flow field and the anode was connected to the fuel container. The active layer of the cathode faced the membrane in all cells. The anode, membrane and cathode were compressed together during cell assembly. The oxygen and fuel (5 M methanol and 4 M KOH) flow rates were 5 sccm and 20 ml min⁻¹, respectively. The fuel cell has an MEA active area of 1 cm².

The electrochemical impedance spectroscopy (EIS) of the cell was measured using an electrochemical workstation (CHI750D, CH Instruments) at open circuit voltage (OCV) with an amplitude of 5 mV and frequencies ranging from 10⁵ Hz to 100 Hz.

The polarization curve of the cell was measured by increasing the current and recording the voltage, which was controlled by a battery testing system (Neware Technology Limited, Shenzhen, China). The cell current was held at 10, 50 and 100 mA cm⁻² and the voltage was recorded to measure the cell durability. The fuel was refreshed approximately every 12 h.

2.6. XRD measurements

The structure of the cathode catalysts was investigated using an X-ray diffractometer (XRD) (D/MAX-3A, Japan) using a Cu K α ($\lambda = 15.444$ nm) source.

3. Results and discussion

3.1. Performance of DMFCs

Fig. 3 shows the performance of the DMFC with PFM and LaNiO₃/CNT and commercial PtRu/C as the cathode and anode catalysts, respectively. We also fabricated DMFCs with classical PEM (Nafion N-117, NRE-211) and the same catalysts and loadings for comparison. A lower cell polarization is observed for PFM at both 20 °C and 65 °C. As shown in Fig. 3a, peak power densities of 28.3 mW cm⁻², 26.6 mW cm⁻² and 20.6 mW cm⁻² are obtained at room temperature for PFM, N-117 and NRE-211, respectively. The performance of the DMFCs with PFM is better than that of the DMFCs with Nafion membranes. Additionally, the DMFCs with

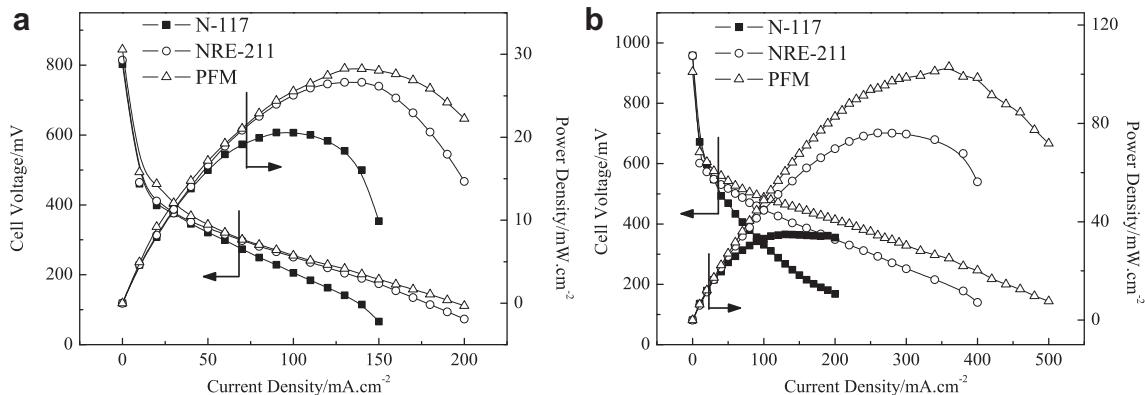


Fig. 3. Current and power output of the cells with various membranes (Nafion N-117, Nafion NRE-211 and PFM). LaNiO₃/CNT and PtRu/C acted as the cathode and anode catalysts, respectively. The tests were performed at (a) 20 °C and (b) 65 °C.

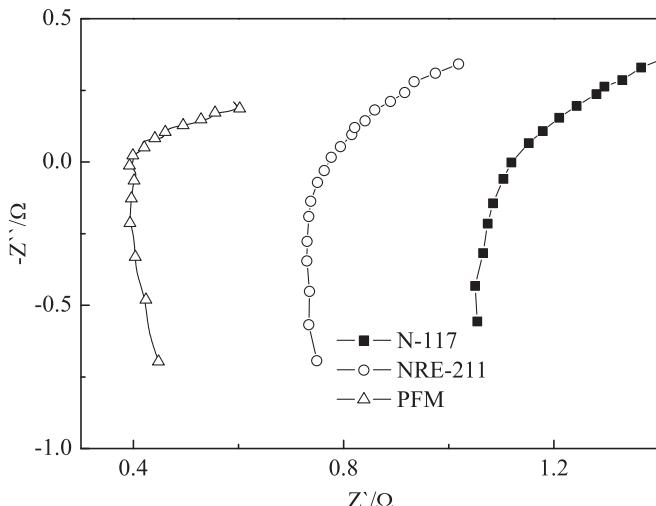


Fig. 4. EIS of the cells using PFM (Δ), NRE-211 (\circ) and N-117 (\blacksquare) membranes as separators. $\text{LaNiO}_3/\text{CNT}$ and PtRu/C were used as the cathode and anode catalysts, respectively. The tests were performed at 20°C .

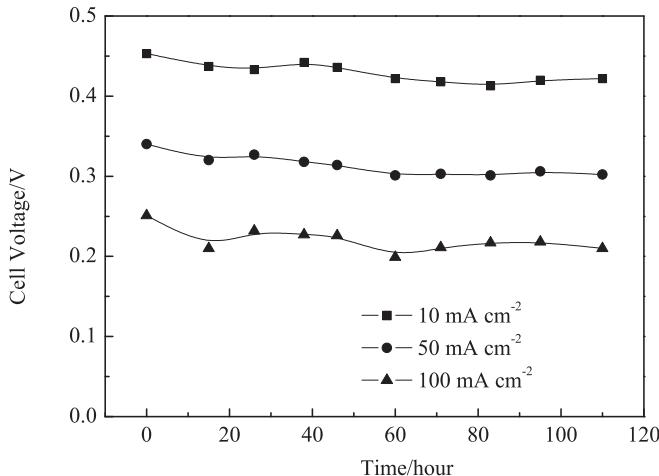


Fig. 5. Comparison of fuel cell durability for various current densities. $\text{LaNiO}_3/\text{CNT}$ and PtRu/C were used as the cathode and anode catalysts, respectively.

NRE-211 show better performance than those with N-117. The performances of the DMFCs at 65°C are shown in Fig. 3b. Peak power densities of 103.0 mW cm^{-2} , 76.2 mW cm^{-2} and 34.8 mW cm^{-2} are obtained for PFM, N-117 and NRE-211, respectively. Again, the DMFCs with PFM exhibit the best performance. Compared with the published work refer to alkaline DMFCs as summarized in Supplemental Material in Table S1, DMFCs with PFM have a good performance not matter used pure oxygen or air (see in Supplemental Material in Figure S1) as oxidant.

3.2. Resistance of DMFCs

EIS was used to explain the differences in the performance of these DMFCs. As shown in Fig. 4, the ohmic resistances, represented by the intercept of the real-axis, are 0.37 , 0.77 and $1.12 \Omega \text{ cm}^{-2}$ for PFM, NRE-211 and N-117, respectively. The DMFCs with PFM have the lowest ohmic resistance, which can be explained as follows. First, ion transfer is more difficult in solid electrolytes (NRE-211 and N-117) than in liquid electrolytes. Secondly, only preferential ions (anions or cations) are allowed to transfer through PEM, but both anions and cations can be used as carriers to transfer through PFM. In addition, N-117 ($183 \mu\text{m}$) is much thicker than NRE-211 ($25.4 \mu\text{m}$). Ions have a longer pathway in N-117 than in NRE-211. Thus, the resistance of N-117 is higher than that of NRE-211.

3.3. Stability of DMFCs

Fig. 5 shows the durability of the DMFCs with PFM for 110 h . The fuel cells are slightly degraded during the tests and the degradation increases with increasing current density.

Which electrodes are responsible for this degradation? First, to determinate whether the cathode catalyst degrades, XRD analysis was performed on the cathodes before and after the durability tests, as shown in Fig. 6a. The results demonstrate that the crystal structure of $\text{LaNiO}_3/\text{CNT}$ does not change after the tests, indicating that this cathode catalyst is stable in methanol/alkaline solution throughout 110 h discharge. However, this information is insufficient to conclude that the cathode does not degrade. Methanol can poison catalyst via a carbon monoxide intermediate, which cannot be detected by XRD measurements. Therefore, the cathode and anode polarizations were measured during the durability tests. As shown in Fig. 6b, the cathode and anode have similar polarization slopes despite the anode being comprised of a noble metal catalyst. During the operation, the cathodic polarization slightly decreases, whereas the anodic

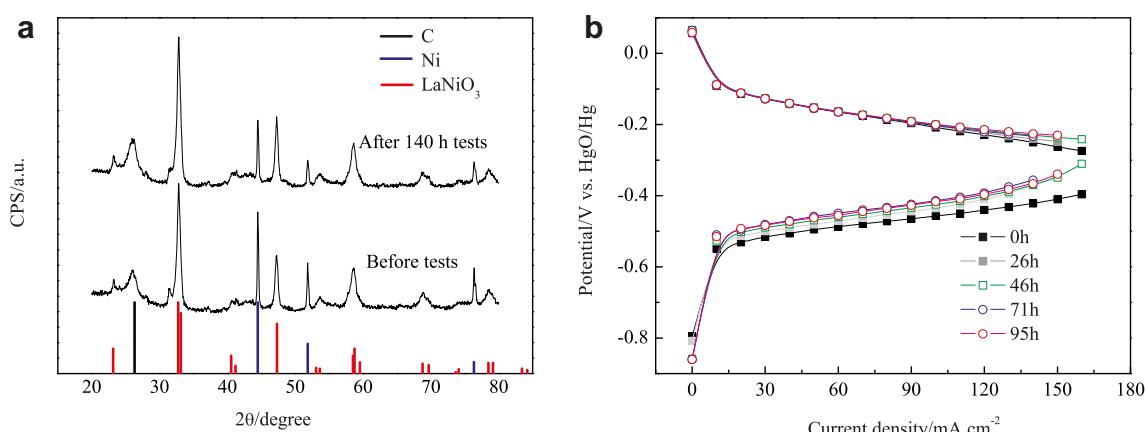


Fig. 6. (a) XRD patterns of cathodes before and after 110 h tests. The nickel XRD pattern corresponds to the nickel foam current collector. (b) Polarization curves for the $\text{LaNiO}_3/\text{CNT}$ cathode and PtRu/C anode.

polarization increases. This finding indicates that the cathode performance slightly improved in the durability test and that the degradation primarily comes from the anode. We can safely conclude that $\text{LaNiO}_3/\text{CNT}$ has excellent durability in the methanol/alkaline fuel solution. Noble metal catalysts are known to experience methanol poisoning, although the poisoning occurs somewhat more slowly for some Pt-alloy catalysts, such as PtRu. This result is in agreement with previous findings that the performance of DMFC with a noble metal catalyst decreased slightly during the durability test [17,18]. The improvement of the cathode durability tests maybe due to the discharge removes impurities and provides better contact between the catalyst and the electrolyte, thus increases the number of activity sites. In conclusion, the $\text{LaNiO}_3/\text{CNT}$ can be used as cathode catalyst in DMFCs with PFM and the degradation of this type of DMFCs is primarily due to the poisoning of the PtRu/C catalyst in the anode.

4. Conclusions

In summary, we have developed a DMFC without using PEM, using PFM as separator membrane instead and $\text{LaNiO}_3/\text{CNT}$ as the cathode catalyst. PFM is much cheaper than PEM and is widely used in Ni-MH battery. Compared with normal DMFCs employing PEM, such as Nafion NRE-211 and N-117, this DMFC is much simpler, easier to assembly and less expensive and has a higher power output. Although the commercial PtRu/C anode is not sufficiently durable, the $\text{LaNiO}_3/\text{CNT}$ cathode demonstrates excellent stability during the 110 h test. Moreover, the cathode slightly improves during the test. We believe that this DMFC with PFM is a promising structure for future applications.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.01.176>.

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